COMBINATION AND DIFFUSION OF GEMINATE RADICALS AND THEIR ACTIVATION VOLUMES.[1,2]

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Our interest in effects of pressure on rates, product distributions and mechanisms of organic reactions in solution has been directed toward detailed studies of free radical reactions.[1,3] The results have suggested the need for a reinterpretation of activation volumes for homolytic scission reactions, and additionally have provided data concerning the effect of pressure on the competitive reactions available to a geminate radical pair such as coupling, disproportionation and separative diffusion.

In contrast to homolytic scission reactions, it is difficult to measure the absolute rate constants for these latter processes because they are quite fast, and data are limited to the effect of pressure on their relative rates. For example, when geminate radicals can combine or diffuse apart (eq. 1), and

$$A\text{-}B \xleftarrow{k_c} \overline{A\cdot\ B\cdot} \xrightarrow{k_d} A\cdot\ +\ B\cdot \qquad (1)$$
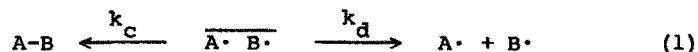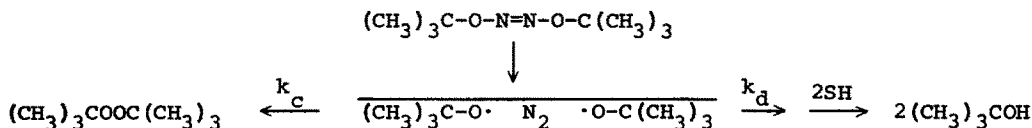
the rate constant ratio k_c/k_d can be determined, the effect of pressure on this ratio gives the difference in activation volumes $\Delta V_d^* - \Delta V_c^*$.[1,3] While such data are useful, it would be much more informative to have access to the individual values of ΔV_d^* and ΔV_c^*. This communication outlines an approach to this problem and our preliminary results.

It is generally observed that k_c/k_d increases with pressure.[1,3,4] This is most certainly due to a simultaneous increase of k_c with pressure (since radical combination reactions should have negative activation volumes) and a decrease in k_d brought about by the increase in solution viscosity with increasing pressure.[4,5] Recently, several groups of workers have been studying the effect of medium viscosity at atmospheric pressure on systems of the general type shown in equation 1 and have demonstrated that the rate constant ratios k_c/k_d increase with increasing viscosity.[6-8] Since it is likely that this is due primarily to a viscosity dependence of k_d, we reasoned that appropriate combination of the results of atmospheric pressure viscosity studies

and those from variable pressure experiments on the same system could permit extraction of the absolute pressure dependence of k_c from the pressure variation of k_c/k_d. This would allow calculation of activation volumes for radical combination (ΔV_c^*).

A system which seemed particularly amenable to such a study was the thermal decomposition (45°) of di-t-butyl hyponitrite (DBH) in a series of hydrocarbon solvents (SH).[6] Traylor and Kiefer demonstrated that the chemistry which occurs is quantitatively described by the series of reactions shown in Scheme I and thus the product ratio (t-butyl peroxide)/(t-butanol)

$$(CH_3)_3C-O-N=N-O-C(CH_3)_3$$

$$(CH_3)_3COOC(CH_3)_3 \xleftarrow{k_c} \underline{(CH_3)_3C-O\cdot \quad N_2 \quad \cdot O-C(CH_3)_3} \xrightarrow{k_d} \xrightarrow{2SH} 2(CH_3)_3COH$$

Scheme I

is equal to the ratio $k_c/2k_d$. The effect of solvent viscosity at atmospheric pressure on log k_c/k_d is shown in Figure 1 (solid points).[6,9] The open points are data which we have obtained from a pressure study on the same system at 45° using n-octane as the solvent.[10] We suggest that the more rapid increase of log k_c/k_d in the pressure study is due to a pressure induced increase of k_c not present in Traylor's study,[11] and thus is a direct experimental demonstration of the negative activation volume for the coupling reaction of two t-butoxy radicals.

Our pressure data alone give the activation volume difference $\Delta V_d^* - \Delta V_c^*$ and combination with Traylor's data allows a determination of the individual values ΔV_d^* and ΔV_c^* (Table I).[12] The activation volume difference $\Delta V_d^* - \Delta V_c^*$ is quite pressure dependent and the individual values of ΔV_c^* and ΔV_d^* suggest that this is due to a pressure dependence of both quantities. Unfortunately, this precludes an accurate graphical extraction of the activation volumes at 1 atmosphere. While methods have been suggested for obtaining such data with strongly curved plots[4,13] we do not believe that our present experimental results justify such analyses. In particular it should be noted that our lowest viscosity data points, determined at atmospheric pressure, do not fall on Traylor's curve. At this time, we cannot offer an explanation except to point out that the values of k_c/k_d at low viscosities in both studies might be expected to have relatively large errors due to the low yields of t-butyl peroxide. Thus we do not wish to firmly commit ourselves to the present quantitative results (Table I), however the qualitative trends encourage us to pursue these studies.
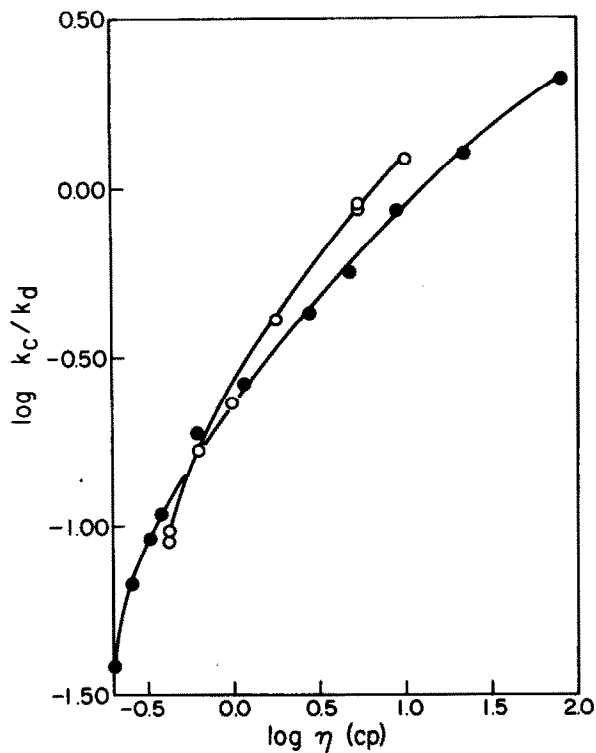
Fig. 1. Plots of log k_c/k_d versus viscosity produced by solvent variation (solid points) and pressure (open points).

Table I

Activation Volumes[a] for Combination and Diffusion of Geminate t-Butoxy Radicals.

P (atm.)	$\Delta V_d^* - \Delta V_c^*$	ΔV_c^*	ΔV_d^*
1	(34)	--	--
500	18.0	-4.2	13.8
1000	16.2	-4.9	11.3
2000	11.6	-2.1	9.5
4000	7.8	-1.5	6.3

a.) Units of cc/mole

References

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8.) a.) W. A. Pryor and K. Smith, J. Am. Chem. Soc., 89, 1741 (1967);
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9.) The viscosity variation was obtained using the solvents n-pentane, n-hexane, n-heptane, isooctane, n-octadecane, Nujol, and mixtures of isooctane and Nujol containing 20, 40, 60, 70, 80, and 90% Nujol.

10.) The low boiling points of n-pentane and n-hexane precluded their use in our studies due to special technical problems associated with the high pressure apparatus. Pressure-viscosity data were unavailable for n-heptane and isooctane. Since such data were available for n-octane[5] it was chosen as the solvent in spite of the fact that it had not been included in Traylor's study.[6] Product ratios were determined by glpc.

11.) Rough calculations indicate that the internal pressures[4] of n-pentane, n-hexane, n-heptane, n-octane and n-decane at an external pressure of one atmosphere are virtually identical (~1400 atm.). Density versus viscosity plots for Traylor's solvents, and for n-octane at various pressures are very similar.

12.) In practice, Traylor's viscosity values were converted to "effective pressures" using viscosity – pressure data for n-octane[5] at 45°. Since k_c is assumed to be independent of viscosity in Traylor's study at atmospheric pressure,[6] the slope of the curve generated by a plot of his values of log k_c/k_d versus these "effective pressures" gives values of ΔV_d^*. The values of ΔV_c^* were obtained by subtraction of these values of ΔV_d^* at several pressures from the values of $\Delta V_d^* - \Delta V_c^*$ (our work) at the same pressures (Table I).

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